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Discrimination of combustion fuel sources using gas chromatography-planar field asymmetric-waveform ion mobility spectrometry

Smoke plumes from cotton, paper, grass, and cigarettes and emissions from a gasoline engine were sampled using solid-phase microextraction (SPME) and samples were analyzed for volatile organic compounds (VOC) using gas chromatography-mass spectrometry (GC-MS). Chemical compositions were sufficiently distinct to allow source identification. Unfortunately, advanced smoke detectors based on GC-MS would be too slow and expensive for most applications. Direct sampling of smoke by atmospheric pressure chemical ionization-mass spectrometry produced a complex response, demonstrating that VOC in smoke were suitable for gas phase chemical ionization. The complexity also indicated the necessity of chromatographic prefractionation. Planar Field Asymmetric-waveform Ion Mobility Spectrometry (PFAIMS) as a capillary GC detector generated chemical information orthogonal to GC retention times. The combination of SPME preconcentration and the additional information provided by the PFAIMS detector yielded unique patterns from smoke from each fuel. Reconstructed ion chromatograms extracted from the PFAIMS scans indicated sufficient resolution of chemical constituents could be completed in less than five minutes with little loss of analytical information. These first measurements suggest that a GC-PFAIMS instrument operating at ambient pressure in air might result in a compact and convenient fuel specific smoke alarm at a reasonable cost.

Original Paper

1 Introduction

The benefits of smoke detectors for protection of human life and property have been known for decades. These detectors are now widely used in domestic, commercial, and industrial structures. Two technologies of measurement are employed in modern consumer grade smoke detectors. One measures ion flux from an alpha source with a Faraday plate collector and the other measures photon flux from a light-emitting diode with a photocell. In both technologies, the diffusion of particles borne on ambient air between the source and the Faraday plate or the photocell is the basis for a positive alarm. Airborne particles interrupt the collection of ions or photons. Conse-

quently, present detectors can not discriminate between smoke sources.

In some instances a false positive alarm is harmless. In others, repeated false alarms can cause a loss in confidence and/or reaction time. Examples of this include false alarms from diesel engine emissions in mine safety [1–3] and in certain naval ships [4–6]. False positives are the focus of this work. False negatives have been addressed by the addition of a gaseous CO sensor to a standard smoke detector since carbon monoxide is generated in most fires [7].

One strategy to bring specificity to smoke detectors is modification of existing technologies. An example is the desensitization of CO sensors using nitric oxide to suppress response to carbon monoxide that arises from diesel engines in atmospheres of underground mines [3]. Thus, the relatively low CO levels from diesel engines did not trigger the alarm and only CO produced at high levels from fires exceeded the response threshold.

The other approach to bring specificity to smoke detectors has been to develop emerging technologies for the detection of volatile organic constituents in smoke. Fires produce a large number of organic compounds in complex

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Abbreviations: APCI, Atmospheric Pressure Chemical Ionization; FID, Flame Ionization Detector; IMS, Ion Mobility Spectrometer; PFAIMS, Planar Field Asymmetric-waveform Ion Mobility Spectrometer; SPME, Solid-phase Microextraction; VOC, Volatile Organic Compound(s).

[1)] Presently in Pittsburgh, PA.

mixtures in the vapor phase as seen in fires from synthetic polymers [8, 9], cigarettes [10–12], and cellulose-based materials such as wood [13]. This approach might in principle provide sufficient analytical information for selective detection of fires through measures of the chemical composition of emissions. However, the analytical performance (resolution or selectivity and detection limits) needed for a practical detector has always been too demanding and complex for most uses.

Sensors whose response is based on solubility and absorptivity of organic compounds on coated surfaces have been examined as replacements for smoke detectors. These include surface acoustic wave (SAW) devices [6] and a polymer-based sensor [5]. The advantage of these sensors is the comparatively low cost and size. Results have shown improved discrimination over conventional smoke detectors for vapors from some materials. The disadvantage of these sensors is that selectivity is based upon principles of general solubility or surface adsorption, thus limiting specificity. A solution to the limited selectivity of such sensors is an array of such sensors with various polymers or coatings. The response then is a complex pattern which can be interpreted using artificial intelligence [4], improving selectivity.

Although a gas chromatograph-mass spectrometer (GC-MS) would provide the specificity needed for complex mixtures of organic compounds, cost and maintenance are prohibitive. Between the performance/cost ratio of a SAW sensor and that of a GC-MS lies ion mobility spectrometry (IMS) technology. Recently, IMS was suggested for use as a smoke alarm [14]. Unfortunately, drift tubes in traditional IMS can be costly [15]. Comparatively low cost drift tubes have become possible with IMS technology [16–20] with micro-machined planar drift tubes of rectangular dimensions 25 mm long $\times$ 5 mm wide $\times$ 0.5 mm deep. These drift tubes have been operated using non-traditional approaches to ion characterization with planar field asymmetric waveform (PFAIMS) dependent mobility methods [16–20]. A limitation commonly encountered with miniature drift tubes is loss in detection limits. This was not observed with the PFAIMS. Detection limits in the range of 0.1 to 1 ng have been obtained [18, 19]. Thus, the most expensive part of an IMS analyzer, the drift tube, now can be mass-produced with concomitant low cost of such analyzers. The size of the analyzer and supporting electronics suggests that this design may be attractive as a detector for a fast gas chromatograph. This may be an affordable replacement for smoke detectors with the added benefit that combustion source material can be identified.

In a high field asymmetric waveform-operated drift tube such as PFAIMS, ions are transported through the planar drift region by a gas flow. Electric fields are applied per-

pendicular to ion transport. Unlike the behavior of ions in traditional IMS drift tubes, ion separation in this drift tube occurs according to ion mobility dependence on electric field strength. The PFAIMS drift tube can be connected to a capillary column and mobility scans can be obtained throughout the chromatographic analysis. This provides chemical information in mobility scans orthogonal to retention time. The small size of the miniature mobility analyzer allows ion residence times of ca. 1 ms, so scan times are 1 s or less.

In a direct comparison between a PFAIMS and a flame ionization detector (FID) a slight broadening in the peak shape was observed that could be attributed to additional column length from connections between the analytical column and the detector. Apart from this small technical effect, the PFAIMS detector provided low cost detection with advanced analytical information for a capillary GC analysis [20].

In this study, smoke from combustion of cotton, paper, grass, tobacco, and gasoline (in an internal combustion engine) were sampled by solid-phase micro-extraction (SPME) and the samples were screened using a GC-PFAIMS. A particular interest was to learn whether this technology had sufficient analytical performance to discriminate between these materials as a first step in equipping cotton warehouses with advanced smoke detectors. Since cotton may smolder for extended periods and spontaneously ignite [21], detecting cotton smoke at very low levels regardless of background combustion byproducts may facilitate the removal of smoldering material before a fire spreads. Under such conditions, speed is not as critical as sensitivity and specificity. Details sought in these studies included: a measure of the chemical vapor composition of several materials using GC-MS; the discrimination of vapor profiles from cotton over those from other cellulose materials by GC-PFAIMS; the identification of chemical markers specific to the burning of a particular material; and what further enhancement of technology should be undertaken to reduce response time and cost.

2 Materials and methods

2.1 Equipment

A model 5880 gas chromatograph (GC) (Hewlett-Packard Co., Avondale PA) was equipped with a HP splitless injector, 25 m SP 2300 capillary column (Supelco, Bellefonte, PA), a flame ionization detector, and a PFAIMS detector [16–20]. The carrier gas was nitrogen (99.99%) scrubbed over a molecular sieve bed. Pressure on the splitless injector was 10 psig with a split ratio of 50:1. Other experimental parameters for the GC included: initial temperature, 30°C; initial time, 5 min; program rate 15° min^{-1}; final

temperature, 200°C; final time, 1 min. The PFAIMS detector was equipped with ca. 0.6–1 mCi of ^{63}Ni. The drift gas was air at 1 to 2 L min^{-1} from a model 737 Addco Pure Air generator (Miami, FL). The drift gas was further purified over a 5Å molecular sieve bed (10 cm diameter × 0.6 m long) and passed through heated stainless steel tubing to warm the drift tube to 70°C. The drift tube was placed against one side of an aluminum box which also included the amplifier and electronics. The analytical column was attached to the drift tube through a 30 cm length of aluminum-clad column and column effluent was carried by drift gas through the ion source region for sample ionization. The drift gas also carried product ions through the gap (0.5 mm) between two flat separating electrodes (5 × 25 mm). Two electric fields were applied to the drift tube: a non symmetric high frequency (1.3 MHz) waveform with a strong electric field (20 kV cm^{-1} peak to peak amplitude) and a weak DC field (−360 V cm^{-1} to +80 V cm^{-1}) of compensation voltage (−18 to +4 V). The signal was processed using a National Instruments board (Model 6024E), digitized, and stored. Excel 97 (Microsoft Corp) and Origin v 5.0 were used to display the results as spectra in topographic plots and graphs of ion intensity versus time.

The GC-MS was a model 5890 A gas chromatograph and Model 5971A mass selective detector (Hewlett-Packard Co., Palo Alto, CA) and was equipped with a 25 m SP 2300 capillary column (Supelco, Bellefonte, PA). The operating parameters of the GC-MS were identical to those for the GC-PFAIMS listed above. Conditions for the MS were: mass range, 45–550 amu; threshold, 500; scan rate, ca. 200 amu s^{-1}; and electron multiplier voltage, 2 100–2 500 according to the automated calibration routine.

2.2 Materials, chemicals, and reagents

Solid-phase microextraction (SPME) fibers and injector were obtained from Supelco (Bellefonte, PA). A mixture of hydrocarbons (hexane to hexadecane) was prepared in methylene chloride solvent at 100 ng/μL per alkane. The alkanes were obtained from various manufacturers and were used as a standard for calibration of chromatographic retention. Materials were all obtained locally and included paper as shredded newspaper; Acala cotton; tobacco as cigarettes; and grass as dried Bermuda grass.

2.3 Procedures

A wad of ca. 9 cm^3 of loosely held material (cigarette excepted) was placed in the end of a borosilicate glass tube (2.54 cm OD × 6 cm long) which was held level and a flame from a butane lighter was used to ignite the sample. The apparatus was placed in a fume hood where flow of

air created air flow through the tube and allowed a sustained but low level burn of the sample over 3–8 min. Hot vapor and particulate emissions from the sample were released in a plume from the sample and the SPME fiber was held in this plume, simulating field sampling of ambient air. The time of sampling was 4 s for cotton, 6 s for cigarettes, 8 s for paper, and 10 s for grass. Samples of engine exhaust from a forklift truck were taken on-site at the Southwestern Cotton Ginning Research Lab in Mesilla Park, NM by holding the SPME fiber in the exhaust stream approximately 0.5 meter from the end of the tailpipe. The samples were freshly analyzed by GC-MS or GC-PFAIMS. In an injection, the SPME was placed in the injection port under splitless mode and held for 30 s until the inlet was switched to split mode. The SPME fibers were conditioned between runs for 10 min at 220°C in nitrogen. Repeatability was obtained by four replicate measurements of cotton burns with 4 s sampling of the smoke plumes. The alkane standard was used to calibrate retention on the GC-MS and the GC-PFAIMS.

3 Results and discussion

3.1 VOC from combustion of fuel sources by GC-MS

A preliminary requirement in this study was to determine if smoke samples taken by SPME methods and analyzed by capillary GC-MS would provided chromatographic profiles for VOCs sufficiently distinct to be attributed to specific fuel sources. Results from GC-MS analysis of SPME samples from four of the five combustion sources (cotton, paper, grass, and engine exhaust) are shown in **Figure 1** as total ion chromatograms. These VOCs spanned the range of carbon numbers from 10 to 18 as shown in retention times for the alkane standard under identical conditions. Time (in minutes) for the alkanes (not shown) were: decane, 4.27; undecane, 5.54; dodecane, 7.00; tridecane, 8.40; tetradecane, 9.81; pentadecane, 11.17; hexadecane, 12.47; and octadecane, 15.79 (alkanes with carbon numbers below 10 were lost in the solvent delay). The traces in Figure 1 spanning 2 to 20 min retention illustrate that all samples exhibited a complex mixture of VOCs from adsorbed aerosols (desorbed in the injection port) and molecular weights for these compounds can be estimated as ca. 150 to 250 amu. Additional chemical information for compounds with molar masses below 150 amu was not sought as such compounds were regarded as too volatile to be collected by SPME sampling methods. Also, no particular effort was made to measure constituents above 250 amu. The emphasis in these measurements was a comparison of emission composition available by SPME sampling without requirements for cryogenic options or ultra high temperatures. Thus, these findings
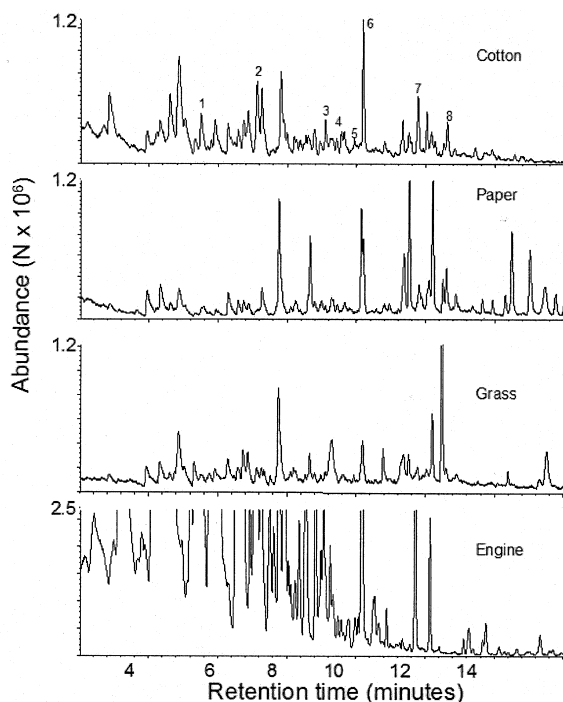
Figure 1. Total ion chromatograms from GC-MS analysis of emissions of organic compounds trapped on SPME fibers by sampling plumes from combustion of several materials. The retention times can be converted to retention indices using an alkane standard as described in the text. Scale factors on intensity were comparable with slight variations as noted.

Table 1. Retention times and ions in mass spectra from peaks that appear distinctive to cotton emissions.

Peak No[a]	Retention time [min]	Prominent ions in order of abundance (base peak abundance)
1	5.51	43 (190,000) 72, 55, 83, 98
2	7.13	42 (180,000), 41, 55, 86, 96
3	9.09	55 (24,000), 126, 41, 42, 43, 53, 69
4	9.55	42 (42,000), 41, 57, 56, 100
5	9.94	43 (19,500), 41, 55, 57, 70, 69, 83
6	10.19	44 (390,000), 57, 43, 41, 128
7	11.78	69 (110,000), 57, 41, 42, 70, 43, 144
8	12.61	102 (54,000), 132, 101, 78, 77, 51, 50

[a]   Refer to Figure 1.

are not a comprehensive chemical characterization of vapors and the measurements were made in anticipation of practical, field-portable instruments which would be engineered for operation under simple conditions.

In the range of molecular weights screened in Figure 1, clear differences existed in the qualitative and quantitative distributions of peaks in the chromatographic profiles. While the profiles of total ion chromatograms appear distinctive in Figure 1, peaks in cotton, paper, and grass were shared in common by these cellulose based materials though differences could be found in relative abundances. An inspection of the chromatograms showed that there were 10 constituents in cotton that were distinctive over all other constituents in other samples and these distinctive components are shown in **Table 1.** In summary, these findings demonstrated that the chemical composition of emissions from burning materials of interest exhibited measurable chemical differences through analysis by high resolution GC-MS. Thus, there is a chemical basis for an advanced smoke detector to discriminate between source materials of fires. Naturally, exhaustive studies on the composition of smoke and reproducibility of sampling and analysis would be needed to further refine these observations. However, precision (discussed below) demonstrated that the differences were not random, encouraging

further study. Ion mobility spectrometers are equipped with an atmospheric pressure chemical ionization (APCI) source and an intermediate step was to determine if the pre-separation could be eliminated from the method. Direct sampling of emissions using an APCI mass spectrometer was made to determine the APCI response to effluent constituents and to measure the resolution possible with a mass spectrometer alone.

3.2 APCI mass spectrometry

The mass spectra from direct sampling of vapors with a corona discharge ion source for grass, cotton and cigarettes are shown for positive ions in **Figure 2** and **Table 2.** In the background air, the reactant ions were ions with m/z 19, 35, 55, 73 amu corresponding to ions of $H_3O^+(H_2O)_n$ with $n = 0,1,2,3$, respectively. Distinctive among these spectra for direct sampling of combustion emissions is that for cigarette smoke where nicotine is evident at m/z 163 amu. Nicotine has a large proton affinity and has been known for decades to yield protonated monomers through reactions as shown in Eq. (1):

$$M + H_3O^+(H_2O)_n \longrightarrow MH^+(H_2O)_n + H_2O \quad (1)$$
vapor   reagent ions   product ions   water
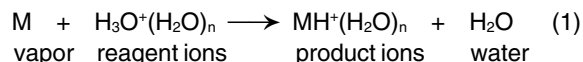
Consequently, nicotine preferentially acquired charge from the reactant ions over other sample vapors and became the dominant ion through competitive charge exchange. Other constituents are present (as shown in Figure 2, bottom) but the nicotine protonated monomer towers above all other peaks in the APCI mass spectrum.

In the other samples, the distribution of vapor concentrations and proton affinities of the VOCs yielded complex mass spectra with masses between 60–200 amu for grass and cotton. These were complex with ions common to each owing to gas phase ionization reactions at ambient pressure. Though multivariate methods might be employed to categorize the sources responsible for the
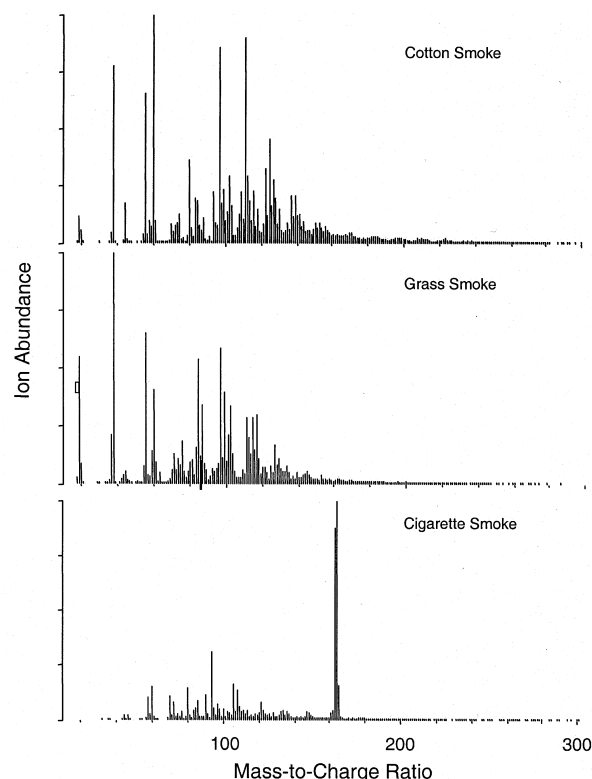
Figure 2. Mass spectra from direct characterization of grass, cotton, and cigarette smoke using atmospheric pressure chemical ionization mass spectrometry.

mass spectra in Figure 2 (top) and Figure 2 (middle), the peaks were separated by unit mass generally in the mass spectrometer (Table 2). The resolution of a mobility spectrometer is inadequate to provide satisfactory separation of such complex ion mixtures. Therefore, pre-separation by capillary GC was regarded as essential. Even with such pre-separation, uncertainty existed over the resolution and performance of a PFAIMS detector with these compounds. Since no predictive models on resolution or separation in PFAIMS yet exist, the method had to be evaluated using the same samples provided to the GC-MS above.

3.3 GC-PFAIMS analysis of VOC from combustion of various materials

Results from GC-PFAIMS analysis of SPME collected samples of combustion emissions are shown in **Figure 3** and **Figure 4** as chromatograms of total intensity of product ions from the mobility scans in comparable format to total ion chromatograms from GC-MS (see Figure 1). Plots are shown for cotton, paper, grass, cigarette, and gasoline engine smoke and the findings reflect the same level of complexity (i. e., number of resolved constituents) as seen above in the GC-MS plots. Here also, as

Table 2. Ion masses from direct sampling of smoke from cigarettes, grass, and cotton with analysis by atmospheric pressure ionization mass spectrometry.

Mass	Cigarettes intensity	Grass intensity	Cotton intensity
37	–	10,064,000	5,420,000
44	–	–	1,210,000
55	–	6,562,000	4,558,000
60	1,070,000	4,050,000	6,978,000
70	732,000	–	–
71	–	1,290,000	–
73	–	1,054,000	–
74	–	–	866,000
75	–	1,812,000	–
80	1,020,000	–	2,532,000
81	–	1,010,000	–
83	–	1,546,000	1,340,000
85	–	5,398,000	1,276,000
87	–	3,416,000	–
88	–	–	728,000
90	782,000	–	–
94	2,144,000	–	1,528,000
97	–	5,890,000	5,960,000
99	–	3,986,000	1,630,000
101	–	2,104,000	–
102	–	–	2,020,000
103	–	3,338,000	–
104	–	–	1,102,000
106	1,134,000	–	–
108	930,000	–	–
109	–	–	1,548,000
111	–	2,874,000	6,284,000
113	–	2,010,000	2,042,000
115	–	2,860,000	–
116	–	–	1,558,000
117	–	2,960,000	–
118	–	–	996,000
123	–	–	2,244,000
125	–	–	3,160,000
127	–	1,694,000	1,912,000
129	–	1,068,000	–
130	–	–	990,000
137	–	–	1,430,000
139	–	–	1,424,000
142	–	–	866,000
164	7,034,000	–	–

expected, the VOCs spanned the range of carbon numbers from 10 to 18 as shown in retention times spanning 3 to 15 min. For the alkane standard (not shown) under identical conditions times (in minutes) were: nonane, 3.54; decane, 4.52; undecane, 5.81; dodecane, 7.24; tridecane, 8.77; tetradecane, 10.27; pentadecane, 11.78; and hexadecane, 13.43. The run was ended before octadecane eluted; alkanes with carbon numbers below nine appeared in a large unresolved peak from 2 to 3.5 min. Previously, GC-PFAIMS was compared to a GC-FID and the chromatographic resolution was seen to be affected
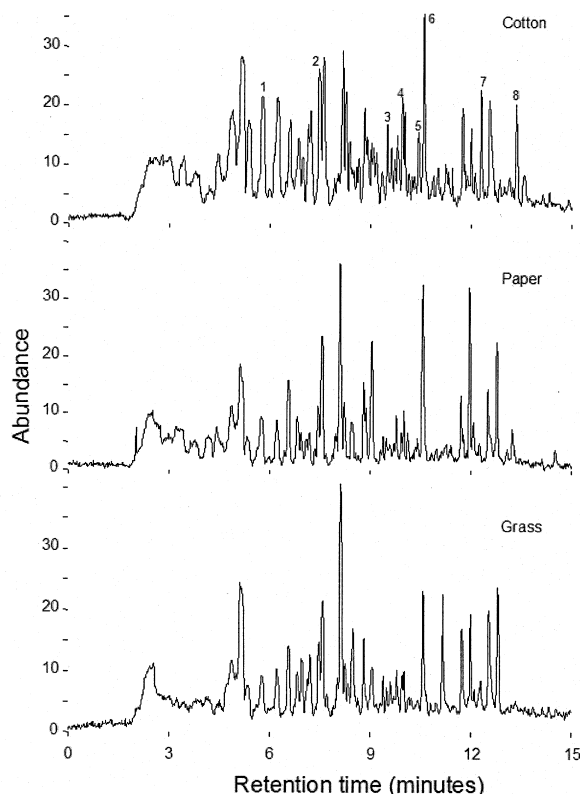
Figure 3. Plots of total intensity of product ions versus retention time from GC-PFAIMS characterization of emissions of organic compounds trapped on SPME fibers in plumes from combustion of cotton, paper, and grass.

slightly from extra column volumes and theoretical plate heights were reduced by ca. 20% [20]. This is now understood to have arisen through additional pipe unions and tubing placed between the analytical column and the detector. Polyimide coated columns should be replaced by aluminum clad columns. Otherwise, trace levels of the polyimide coating on the outer surface of the capillary column lead to impurities with high proton affinities in the ion source and an amine or imide based reagent ion. A bare aluminum clad column avoided this but also introduced a small amount of extra-column volume. However, this slight degradation in overall chromatographic efficiency observed previously was not apparent in the results presented here.

Differences were observed in relative abundances of constituents within the chromatograms between Figure 2 and those in Figure 3 and Figure 4. This is associated with differences in response factors between mass spectrometry and ion mobility spectrometry or differences between vacuum based ion formation and ionization at atmospheric pressure. In the latter, response is roughly approximated by proton affinities of molecules. Thus, what appear as minor constituents in emissions from cot-
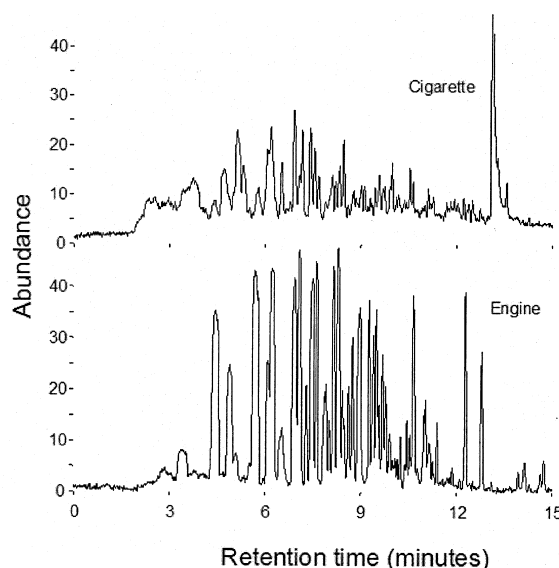

Figure 4. Plots of total intensity of product ions versus retention time from GC-PFAIMS characterization of emissions of organic compounds trapped on SPME fibers in plumes from combustion of cigarette and engine exhausts. Plots can be compared directly to Figure 3.

Table 3. Reproducibility of combustion experiments including sampling, GC-MS determination, and data reduction. Measurements were made using 4 s burns of cotton with four complete replicate experiments.

Retention time (min)	Area	Standard deviation	% Relative Standard deviation (%RSD)
2.9	20 696 587	5 188 474	25.07
5	26 439 681	5 973 165	22.59
8	19 698 838	6 011 899	30.52
11.8	12 360 466	3 020 822	24.44
12.7	10 095 391	1 749 393	17.33
14.02	3 873 334	1 167 082	30.13

ton between 8 to 10 min (Figure 1) appear as significant constituents at the same retention time in Figure 3. In cigarette smoke, nicotine dominated the PFAIMS chromatographic response (Figure 4) as it did the MS trace (Figure 2). On the other hand, the response to small molecules from C10 to C14 by PFAIMS (Figure 4) was clearly more pronounced than that from MS (Figure 2).

Reproducibility was determined using the peak heights on the product ion plots of Figure 3 and Figure 4 and results are shown in **Table 3** for several peaks from throughout the elution program. The relative standard deviation of the measurement was ranged across a comparatively narrow gap from 17 to 30% RSD. This variation included all aspects of sample preparation, sampling, measurement,
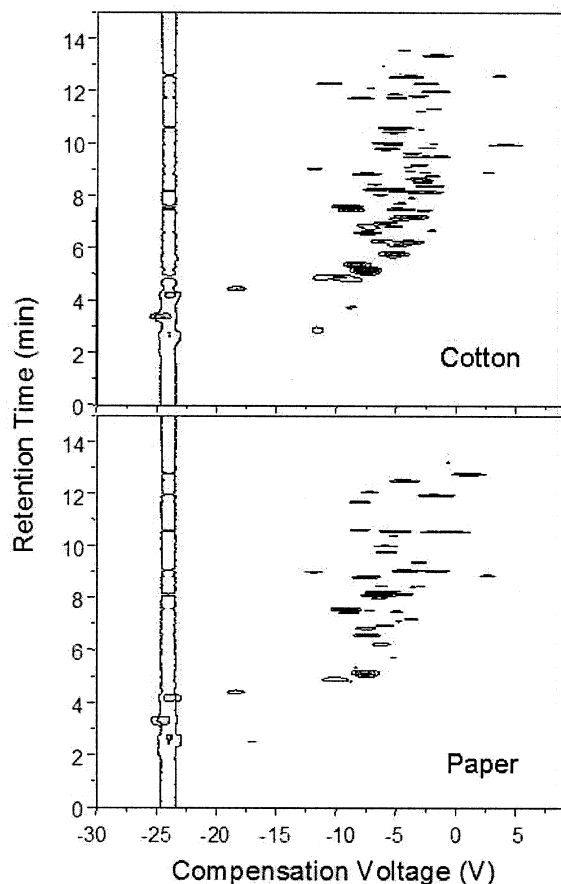
Figure 5. Topographic plots from GC PFAIMS characterization of emissions of organic compounds trapped on SPME fibers in plumes from combustion of cotton and paper.

Figure 6. Topographic plots from GC-PFAIMS characterization of emissions of organic compounds trapped on SPME fibers in plumes from combustion of grass and gasoline.

and automated data reduction. As a consequence, results from this method exhibited actual differences that could not be attributed to variance or random error even though sampling was made with comparatively casual attention to the limitations of SPME.

The peaks unique to cotton were labeled in Figure 1 and Figure 3 and summaries of the mass spectral properties for these are shown in Table 1. The GC-PFAIMS results could be compared directly to the findings from GC-MS and certain peaks were found in the cotton to be unique or special to cotton combustion. These are labeled in Figure 3 and mass spectral properties are listed in Table 2. Identification was not attempted here as authentic standards were lacking. The 2D plots are particularly good for quantitative measures but do not disclose the analytical value of orthogonal information available in the mobility scan. This can be seen in the topographic plots of **Figure 5** and **Figure 6.**

Topographic plots from GC-PFAIMS analysis of all samples demonstrated that information in the mobility scan provides distinctiveness for each sample. The most dis-
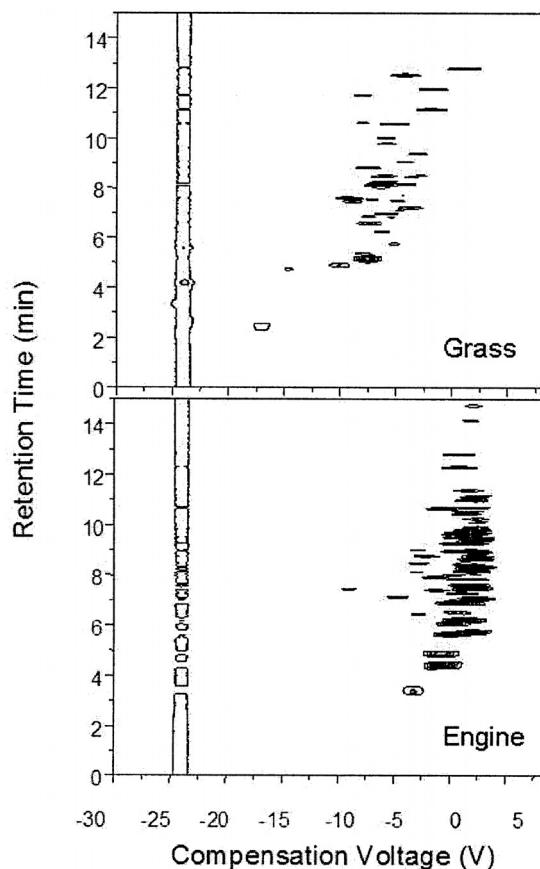
tinctive of the plots shown in Figure 5 and Figure 6 is that from the internal combustion engine where incompletely combusted hydrocarbons appear in a narrow band of compensation voltage from -2 to 2 V. This was consistent with mass spectra and with the alkane standard with peaks of similar compensation voltage. Plots for the cellulose materials (cotton (Figure 5), paper (Figure 5), and grass (Figure 6)) exhibited some common features with peaks from 5 to 14 min evenly distributed and compensation voltages that spanned -10 to $+5$ V. In general, the compensation voltage trended from -10 V toward 0 V with increasing retention time. There will be a concentration dependence that may alter the appearance of the topographic plot so the user may have some control of the appearance of these plots based upon graphic thresholds. An attempt was made here to scale results for comparative intensity and so findings would not be biased or skewed. Still, the results were promising as a first examination of the concept of GC-PFAIMS as an advanced smoke detector. Specific to the goals of this project, cotton exhibited unique or characteristic peaks in the 3D plots as labeled in Figure 5 and Figure 1.
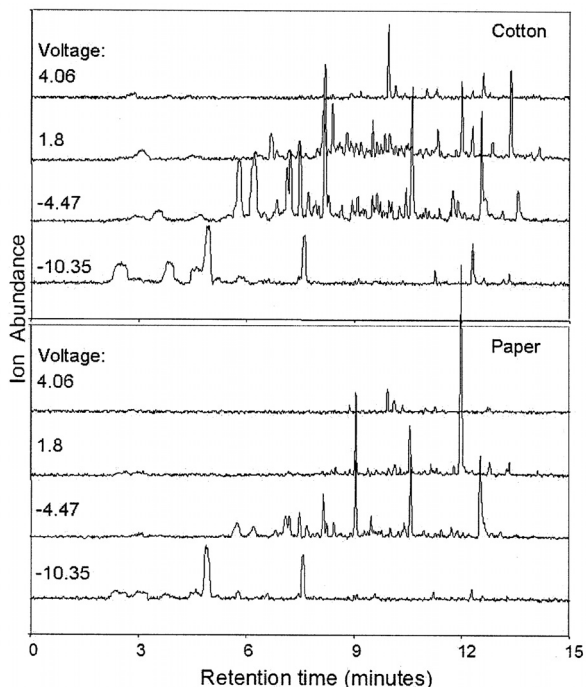
Figure 7. Plots of ion chromatograms extracted from analyses by GC PFAIMS of emissions from combustion of cotton (top frame) and paper (bottom frame). Ion chromatograms were extracted from plots in Figure 5.
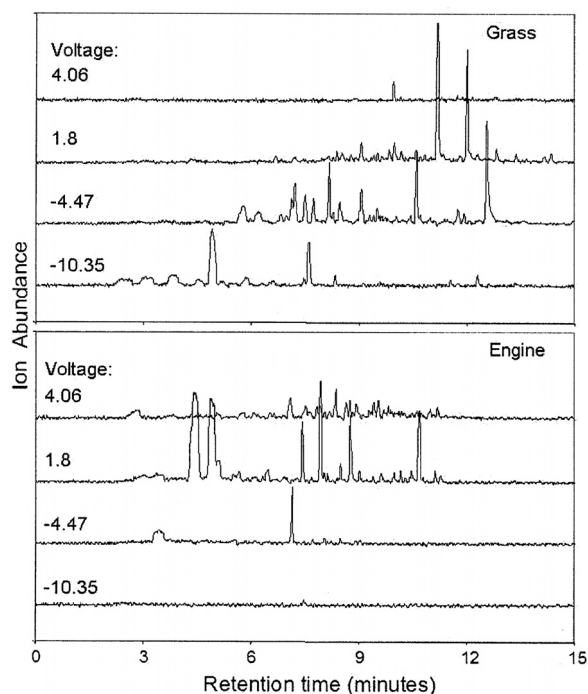

Figure 8. Plots of ion chromatograms extracted from analyses by GC PFAIMS of emissions from combustion of grass (top frame) and from engine exhausts (bottom frame). Ion chromatograms were extracted from plots in Figure 6.

All of these results had been obtained using comparatively slow GC temperature ramps. The 15 min might be reduced substantially with a fast GC. An essential question is what information is available in the plots and to what degree can this information be compressed without losing measurement resolution beyond a usable condition. In mass spectrometry, selected ion monitoring is used to improve detection limits and can add selectivity through ion ratio measurements. This same concept can be applied to PFAIMS to monitor certain ions. This approach to measurement may be the best route to fast chromatography (**Figure 7** and **Figure 8**).

3.4 Simplification of the approach

In Figure 7 and Figure 8, plots of ion intensity at four compensation voltages (4.06 V, −1.8 V, −4.47 V, and −10.35 V) are shown top to bottom in each frame for cotton (Figure 7), paper (Figure 7), grass (Figure 8) and gasoline engine exhaust (Figure 8). With this approach which is analogous to ion chromatograms in GC/MS measurements, certain regions of compensation voltage were graphically extracted from the matrix of retention time, compensation voltage and ion intensity. A measure of the amount of chemical information in the selected ion mobility plots from GC-PFAIMS can be seen in these figures where differences in samples are further accentu-

ated. These patterns are distinct and suggest that selected ion plots allow a route to chemical identification where information can be compressed through fast chromatography. A further possibility is forming ratios of two or more extracted ion chromatograms (not done here). The findings in Figure 7 and Figure 8 demonstrate that adequate resolution of peaks is available in these complex patterns to compress the chromatographic time scale. At present the scan time of 1 s may be too slow for below 3 min. Since the ion residence time in the drift tube is 1–2 ms, ion hopping could occur for a set of ions in 40 ms, (4 ions for 10 ms each). Thus, high speed GC where the complete separation occurs in 60 s would allow 1000 cycles throughout the measurement. The time resolution of 1 part in 1 500 would be comparable to the current value of 1 in 960. Thus, should all other facets of separation be scalable, the drift tube with ion hopping should allow high speed GC-PFAIMS as a realistic smoke detector to distinguish sources of smoke. In order to achieve high speed GC-PFAIMS, band broadening from extra-column volume (post column tubing and fittings) will need improvements.

4 Conclusions

The combination of a GC with a PFAIMS provided analytical capability to distinguish the source of combustion of

several materials through analysis of vapors sampled by SPME. Topographic profiles of ion intensity versus retention time and compensation voltage provided orthogonal information to the GC separation useful in chemical recognition of the sources of combustion. Ion monitoring could be used with compression of the retention scale from the present 15 min to approximately 2 min. The advent of high speed small gas chromatography coupled with the micromachined drift tubes should provide an advanced smoke detector of comparably high analytical performance at an affordable cost. These findings demonstrated that the chemical composition of smoke from sources of interest exhibited measurable chemical differences through analysis by high resolution GC-MS. A remarkable level of reproducibility for complex chemical process (i.e., combustion of natural materials) was obtained using simple sampling methods. While this supports the further development of this approach for smart smoke detectors, additional support on the changing vapor composition with time of burn and detailed identification of volatile products from combustion are needed.

Acknowledgments

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